USING OPTICAL PROPERTIES OF DISSOLVED ORGANIC MATTER TO DISCRIMINATE SEWAGE TREATMENT EFFLUENTS FROM RUNOFF IN SANTA MONICA BAY, CALIFORNIA

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Using Optical Properties of Dissolved Organic Matter to Discriminate Sewage Treatment Effluents from Runoff in Santa Monica Bay, California

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The Hyperion Treatment Plant (HTP) located off Santa Monica Bay is the largest sewage treatment facility in the Los Angeles Metropolitan Area. In order to perform necessary repairs chlorinated secondary-treated effluents were temporarily diverted from the 5-Mile Outfall to the 1-Mile Outfall. To monitor the environmental impacts, the city of Los Angeles established a program. My project assisted with distinguishing effluent dissolved organic matter (DOM) from terrestrial-runoff DOM based on chemical analysis, and optical properties of DOM. Samples were collected weekly during Fall 2015 and were analyzed for CDOM absorption spectra (250-700 nm), EEM fluorescence, concentrations of dissolved organic carbon and total dissolved amino acids. This data set complemented existing water quality analysis products, and provided critical data for the development of remote sensing approaches.

DEDICATION

I would like to dedicate my thesis to my parents who have given me more than I ever needed and supported me throughout my whole life. Love you Mom and Dad.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Kaiser, for his guidance and support throughout the course of this research.

Thanks also go to my friends and colleagues for all their encouragements and support during those long nights. I would also like to thank Aggies Commit to Excellence Scholar (ACES), Texas Sea Grant, and the Undergraduate Thesis Scholar programs for giving me the opportunity to do research.

CHAPTER I

INTRODUCTION

Measurement of specific optical and chemical parameters provide useful tools to elucidate sources and transformations of dissolved organic matter (DOM) and track water quality (Coble, 2007 & Helms et al., 2008). In this thesis, optical and chemical measurements are employed to track sources of DOM in the Santa Monica Bay, California during discharge of sewage about 1 mile away from popular and heavily frequented beaches.

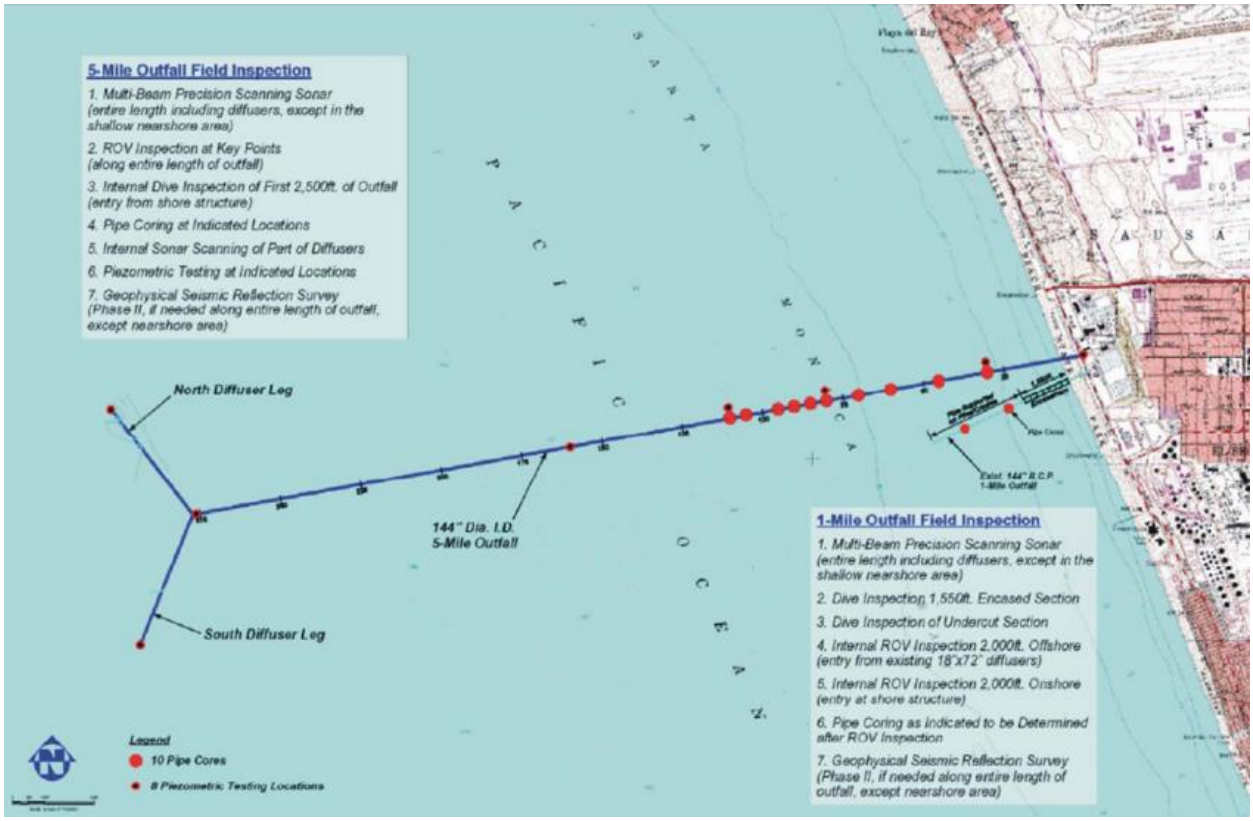

Figure 1. The 5-Mile and 1-Mile outfall of the Hyperion treatment plant. Picture obtained from the Southern California Coastal Ocean Observing System (SCCOOS) website for the Hyperion Outfall Diversions Project

The Hyperion Water Reclamation Plant diverged effluent from a 5-mile Outfall to a 1-Mile Outfall due to necessary repairs on the 5-Mile Outfall. Figure 1 shows a map of the 5- Mile and 1-Mile Outfall.

During diversion of sewage the City of Los Angeles implemented a rigorous and extensive monitoring program to observe effluent spreading and ensure the protection of public health. Effluent monitoring included a variety of components including toxicity testing, extensive measurements of various chemicals (eg. Pesticides, metals), nutrients, DOM parameters, and monitoring of microbial abundances (bacteria, phytoplankton, etc.)

DOM is a critical component of modern biogeochemical cycles, containing as much total carbon as the atmosphere, contributing to the majority of carbon flux from terrestrial to marine environments, and fueling microbial food webs in all aqueous environments. DOM processing occurs on timescales varying by several orders of magnitude, with photodegradation and redox reactions on the order of microseconds, while degradation-resistant DOM can circulate in the ocean for thousands of years (Dittmar and Paeng, 2009; Loh et al., 2004; Druffel et al., 1992). Understanding DOM cycling is important for water quality issues and maintaining healthy ecosystems.

Detailed information on DOM sources can be gained from measurement of optical parameters such as chromophoric dissolved organic matter (CDOM) absorbance and fluorescence, and specific chemical biomarkers. CDOM comprises a specific fraction of DOM that absorbs light over a wide range of UV and visible wavelengths. Chemically, this DOM is not easily defined and includes a complex mixture of organic compounds with functional groups capable of adsorbing UV and visible light. Although CDOM is not well defined, CDOM absorbance and fluorescence measurements have been extensively used in aquatic settings to examine the fate of DOM and to distinguish its sources (Coble 2007, Fellman et al. 2010). CDOM parameters including the fluorescence index (FI) and specific UV absorbance at 254 nm ($SUVA_{254}$), for example, are routinely utilized to assign DOM sources in a broad range of aquatic science studies. As

fluorescence index values increase this is routinely interpreted as increasing microbial contribution to DOM (McKnight et al. 2001, Cory and McKnight 2005), and conversely as $SUVA_{254}$ values increase this is often interpreted as reflecting a greater contribution from allochthonous sources (Neff et al. 2006, Yamashita et al. 2008).

Measurements of chemical biomarkers are uniquely suited to establish distinct sources of DOM as well as transformation reactions. For example, lignin is a major structural polymer found only in vascular plants, making lignin phenols useful tracers of terrigenous organic matter in the marine environment (Hedges and Mann, 1979).

Biomarkers and optical indicators together assess the degradability of DOM in aquatic environments. Most approaches for characterizing degradability and diagenetic state rely on compositional changes in organic matter that result from microbial decomposition. Freshly produced organic matter is characterized by high carbon-normalized yields of amino acids (AAs) and neutral and amino sugars (Cowie and Hedges 1992, 1994, Biddanda and Benner 1997, Benner and Kaiser 2003). Carbon-normalized yields of these common biochemicals are good indicators of organic matter ‘‘freshness” and diagenetic state because these compounds are preferentially utilized during biodegradation (Keil et al. 2000, Amon et al. 2001, Amon and Benner 2003, Benner 2002).

In addition to the application of carbon-normalized yields of compounds as diagenetic indicators, there is a growing understanding of the relationship between molecular composition and reactivity. The relative abundance of individual amino acids is altered during decomposition in a fairly predictable manner, a phenomenon that has been used to describe the relative diagenetic state of organic matter (Dauwe and Middleburg 1998, Dauwe et al. 1999, Lee et al. 2000, Yamashita and Tanoue 2003). Recent studies have also suggested that the relative

abundance of individual neutral sugars in DOM could be useful as diagenetic indicators (Amon et al. 2001, Kirchman et al. 2001, Kaiser and Benner 2009). The relative abundance of the amino sugars glucosamine (GlcN) and galactosamine (GalN) has been used as a diagenetic indicator, as well as source indicator (Liebezeit, 1993, Dauwe and Middleburg 1998, Benner and Kaiser 2003, Kaiser and Benner 2009). The ratio of GlcN:GalN is relatively high (>8) in organic matter enriched in chitin and decreases during biodegradation (Liebezeit 1993, Müller et al. 1986, Benner and Kaiser 2003). Relatively low (<2) GlcN:GalN values are indicative of diagenetic alteration and a bacterial source (Liebezeit 1993, Ogawa et al, 2001, Benner and Kaiser 2003).

An extended goal of this project was the creation of a remote sensing approach that will allow tracking of DOM sources on wide spatial and temporal scales. Remote sensing approaches allow real time monitoring and as such represent an ideal tool for quick response decisions needed in case spill events occur. The remote sensing approach is outside the scope of this thesis, but data presented here will provide the foundation for development of appropriate algorithms.

CHAPTER II

METHODS

Samples were collected as part of the Hyperion Water Reclamation Plant: Effluent Pumping Plant Header Replacement Project in Santa Monica Bay, California from September 16th to December 2nd 2015. Sampling trips were repeated weekly at a set number of stations along the coast and in close proximity to the outfall of the sewage pipe. Per trip 12-15 samples were collected. The sample locations are represented in Figure 2. After collection, samples were stored cold over ice and shipped to the lab for further processing.

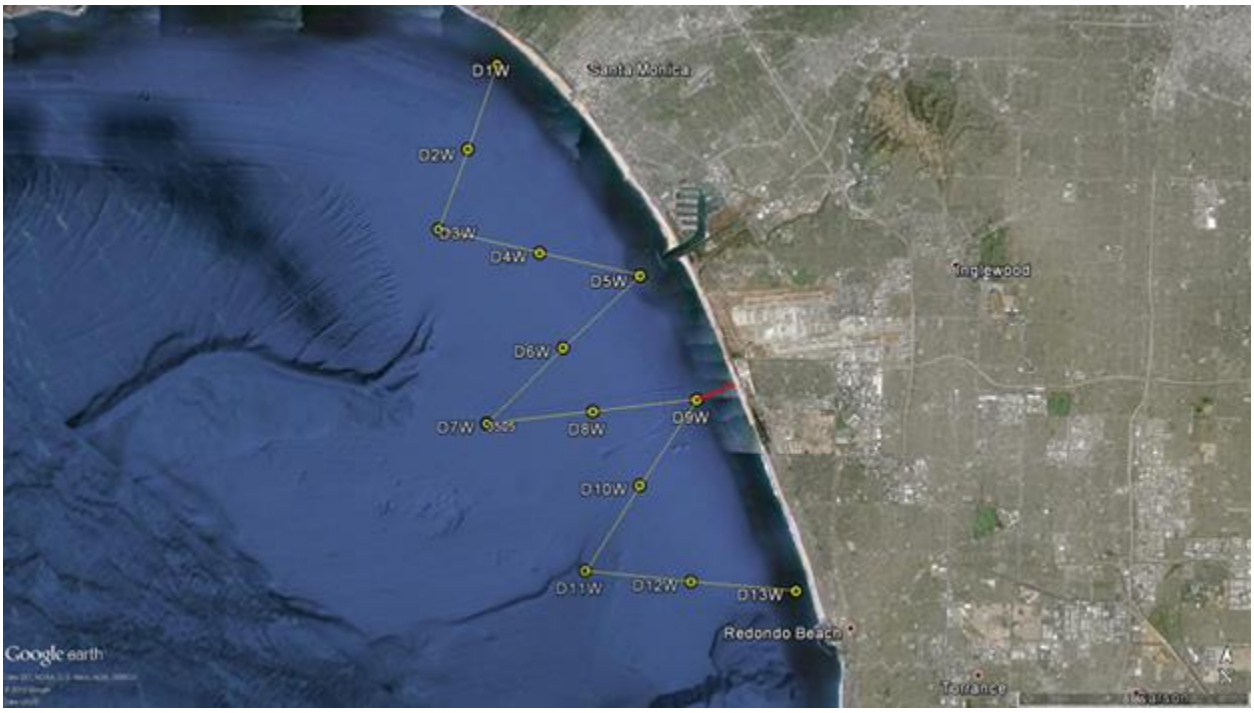

Figure 2. Map plotting the sample locations. Picture obtained from the SCCOOS website for the Hyperion Outfall Diversions Project.

Upon arrival, optical characteristics including CDOM absorption spectra (250-700 nm) and emission excitation matrix (EEM) were recorded. EEM fluorescence spectra were obtained on a PTI fluorometer, and absorbance spectra were measured on a Beckmann UV spectrophotometer. CDOM absorption was measured in 30 mL quartz cuvettes. A blank was run

before each sample group containing deionized water (Helms et al., 2008 & Coble, 2007). For the EEMs, each run used 1 mL of the sample in a 1x1 cm quartz cuvette (Huguet et al., 2009 & Coble, 2007).

Concentrations of DOC were analyzed using a high-temperature combustion analysis with a Shimadzu TOC-V instrument (Benner and Strom, 1993). DOC samples were acidified to pH 3 to remove inorganic forms of carbon prior to analysis.

Total hydrolyzable amino acids (THAA) were analyzed using high-performance liquid chromatography (HPLC) on an Agilent 1260 Infinity LC system according to Kaiser and Benner, 2005. Before chromatography, samples were first hydrolyzed by microwave-assisted vapor phase hydrolysis. All samples were treated as followed for the hydrolysis. Samples were first thawed out. Then in a 2-mL Agilent vial, 1 mg of ascorbic acid was measured and dissolved in 1 mL of MiliQ water. In another Agilent vial, 1 mL of the sample was spiked with 10 μL of the ascorbic acid solution. Then 100 μL of the spiked sample were transferred to an insert and dried under nitrogen. Inside each vessel, the inserts were placed in order starting with a marked insert with the max capacity of ten inserts. Once all the inserts were placed inside the vessels, each vessel was filled with 5 mL of 6 M HCl. All vessels were tightly closed before taken to the microwave. After hydrolysis, residual acid was dried off with a stream and nitrogen, and hydrolysates were redissolved in 100 μL of 0.01 mol L^{-1} borate buffer at pH 9.6. Analyses include blanks, standards, and samples.

CDOM absorption and fluorescence data was used to calculate specific optical and chemical parameters: $SUVA_{254}$, Fluorescence-Index, BIX, spectral slope ($S_{275-295}$), slope ratio (S_R), and concentration of lignin phenols. Correction of absorbance spectra was performed by an exponential fit of absorbance data and calculation of an offset value that was subtracted from the

spectrum (Fichot and Benner, 2011, Fichot et al., 2106). The corrected absorbance data were used to calculate the Naperian absorption coefficient, $a_g(\lambda)$ (m^{-1}).

$SUVA_{254}$ was calculated according to:

$$SUVA_{254} = A_{254}/DOC \text{ (L mg}^{-1} \text{ m-}^{1}) \quad (1)$$

where A_{254} is the absorption at 254 nm, and the DOC was obtained from the DOC analyzer. $SUVA_{254}$ has been used as a parameter to estimate the relative contribution of aromatic structures in DOC (Weisshaar et al., 2003). High $SUVA_{254}$ are observed in DOC derived from terrestrial environment reflecting the aromatic structures derived from vascular plants and various other sources.

The Fluorescence index, FI, was calculated from EEM data as follows:

$$\text{Fluorescence index (FI)} = \lambda_{em} \text{ 450nm} / \lambda_{em} \text{ 500 nm at } \lambda_{ex} \text{ 370 nm} \quad (2)$$

using the emission at 450 nm divided by the emission at 500 nm at the 370 nm excitation wavelength. A value of 1.9 for FI indicates an aquatic and microbial source while a value around 1.3 indicates a terrestrial and soul source (McKnight et al., 2001).

The BIX index was calculated according to:

$$\text{BIX} = \lambda_{em} \text{ 380nm} / \lambda_{em} \text{ 430 nm at } \lambda_{ex} \text{ 310 nm} \quad (3)$$

utilizing the emission at 380 nm divided by the emission at 430 nm at the 310 nm excitation. For BIX values, a value around 0.6 to 0.7 correlates with a low autochthonous component, a value around 0.7 to 0.8 is for an intermediate autochthonous component, a value around 0.8 to 1 represents a strong autochthonous component, and a value higher than 1 belongs to a biological or aquatic bacterial origin (Hueguet et al., 2009).

Spectral slope coefficients between 275 and 295 nm were calculated by a linear fit of the log-linearized $a_g(\lambda)$ interval of the respective spectral range. Helms et al. (2008) showed that spectral slope responds to aromaticity of DOM and molecular weight.

Lignin was calculated according to:

$$\ln(TDLP_9) = -2.282 * \ln(ag(350)) - 8.209 * \ln(ag(275)) + 11.365 * \ln(ag(295)) + 2.909 \quad (4)$$

where ag(ʎ) is the Naperian absorption coefficient at 275 nm and 295 nm (Fichot et al., 2016).

Finally, the slope ratio was determined as follows:

$$\text{Slope ratio } (S_R) = \text{275-295 nm slope} / \text{350-400 nm slope} \quad (5)$$

where the slope coefficients between 350 and 400 nm were calculated analogous to the slope coefficient between 275 and 295. The slope ratio was described as an indicator of shifts in molecular weight and photobleaching (Helms et al., 2008). Slope ratios tend to be lower in freshwater samples compared to the values found in the marine environment indicating a lower degree of photobleaching in freshwater systems.

In addition to optical measurements on discrete water samples, in-situ sensors tuned to optical properties of chlorophyll and CDOM derived from terrestrial sources were deployed during sampling. In-situ sensors included SeaBird Wetstar models specifically an ECO-AFL fluorometer, and a Wetstar CDOM fluorometer,

CHAPTER III

RESULTS

The data was grouped into three stages—pre-diversion, during diversion, and post-diversion— to show changes of optical parameters and measured biochemicals. In addition, detailed data is presented in Table 1. Salinity was variable between the different stages but a freshening was clearly visible during the diversion close to the 1-Mile Outfall with a clear trajectory toward the coast (Fig.3). Oxygen and DOC concentrations also showed changes between the three stages (Fig. 4, 5). DOC concentrations exhibited localized peaks close to shore during the diversion possibly derived from run-off sources (Fig. 5B).

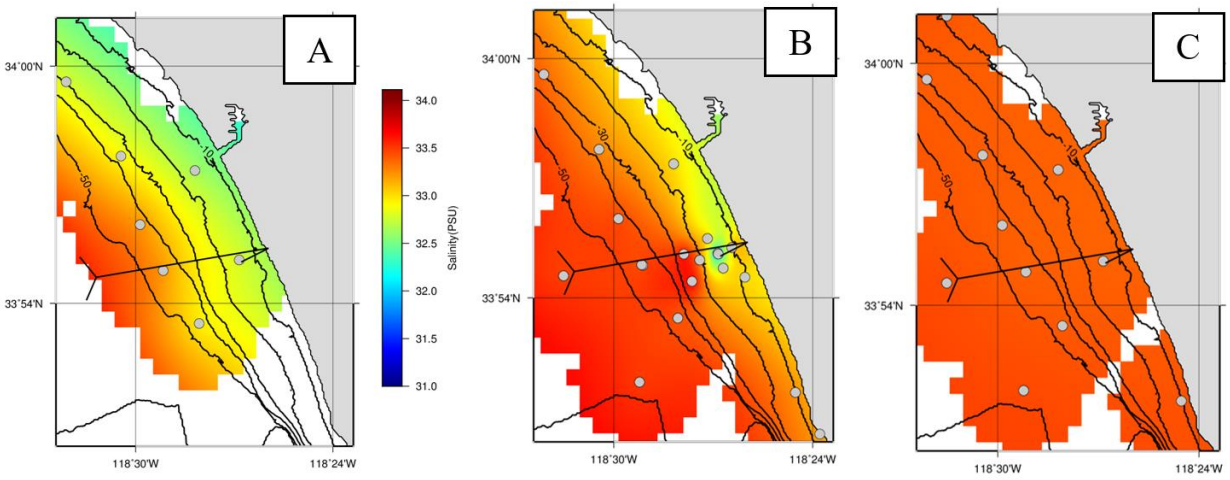

Figure 3. Salinity values obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

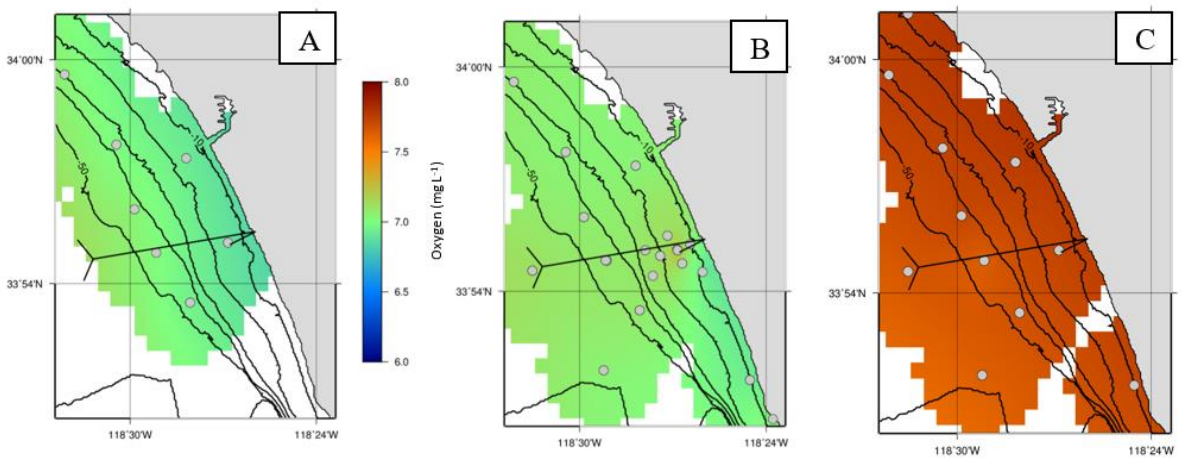

Figure 4. Oxygen concentrations obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

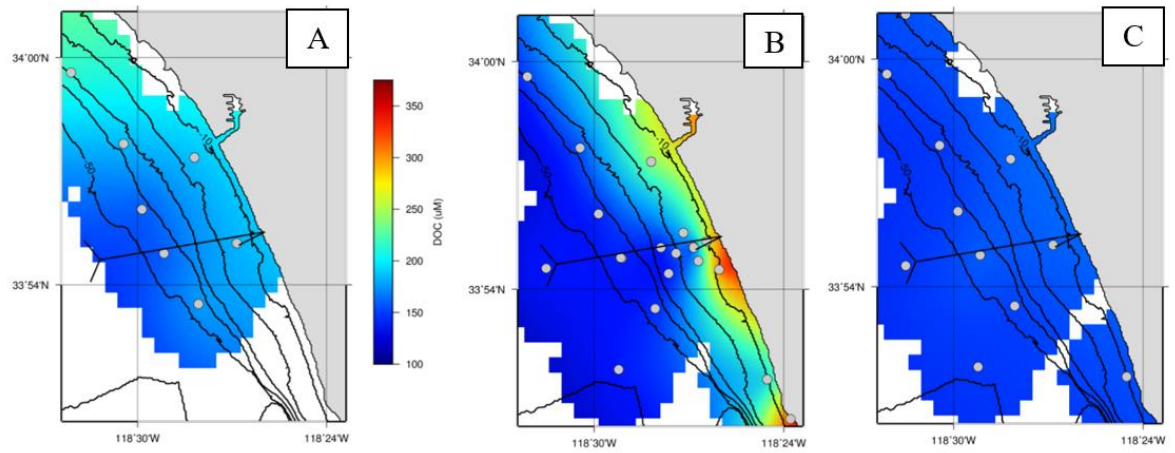

Figure 5. DOC concentrations obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Prediversion stage, B) Diversion stage, and C) Post-diversion.

Nutrient concentrations—ammonium, nitrate, phosphate—were generally low but ammonium and phosphate concentration increased almost ten-fold during the diversion event in close proximity to the sewer outlet (Figs 6,7, 8). Data for nutrient concentrations were provided by Dr. Cedric Fichot (Boston University) and presented a core component of the monitoring program.

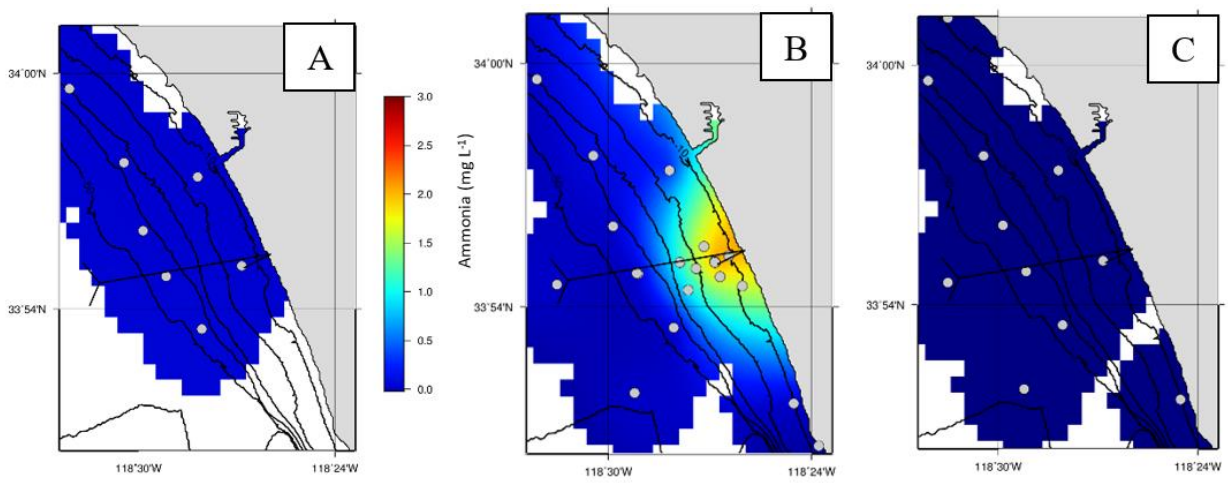

Figure 6. Ammonium concentrations obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

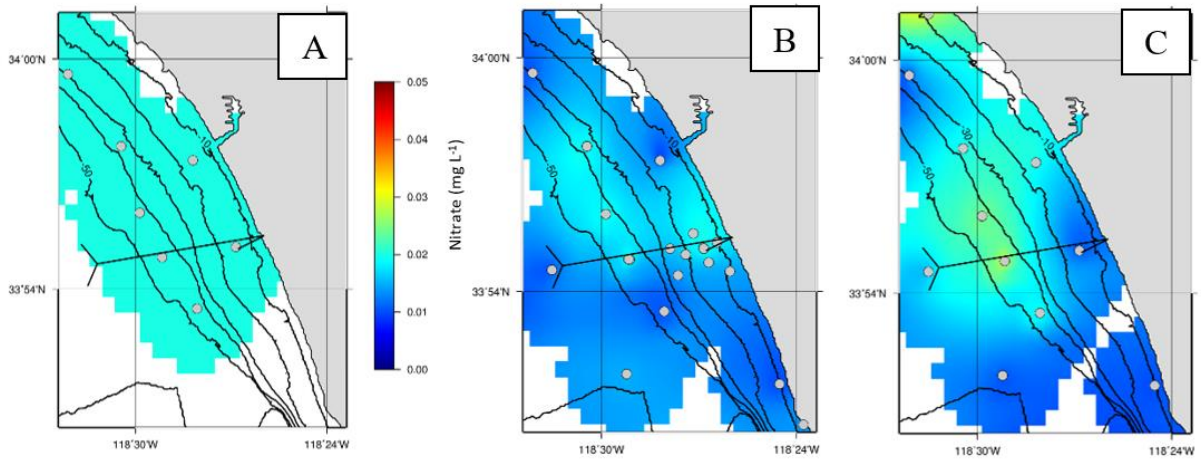

Figure 7. Nitrate concentration obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Prediversion stage, B) Diversion stage, and C) Post-diversion.

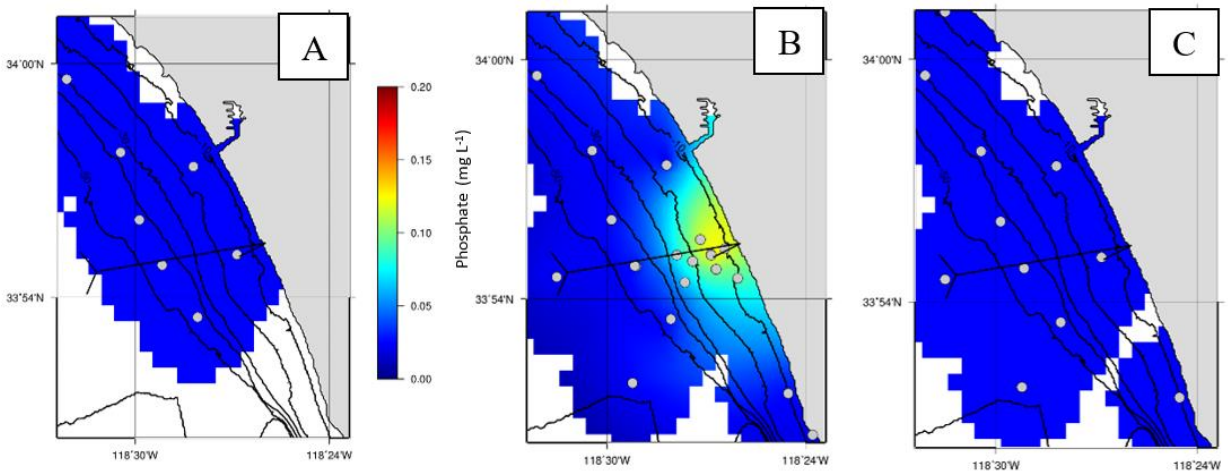

Figure 8. Phosphate concentration obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

Chlorophyll concentrations were low before and after the diversion, but showed a dramatic increase during the time of diversion (Fig. 9).

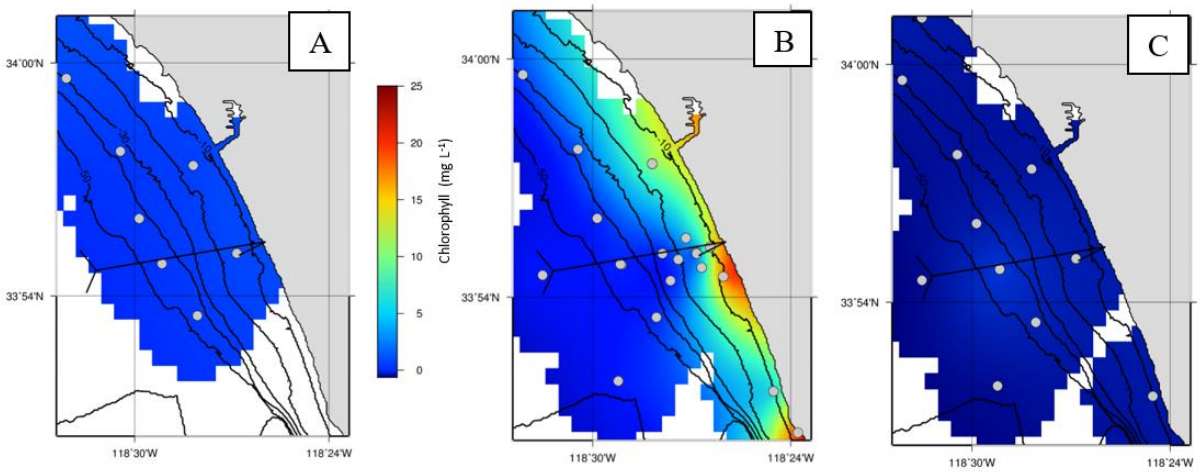

Figure 9. Chlorophyll concentration obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Prediversion stage, B) Diversion stage, and C) Post-diversion.

Chemical and optical parameters for DOM included THAA, calculated values for lignin and $SUVA_{254}$, and specific fluorescence coefficients.

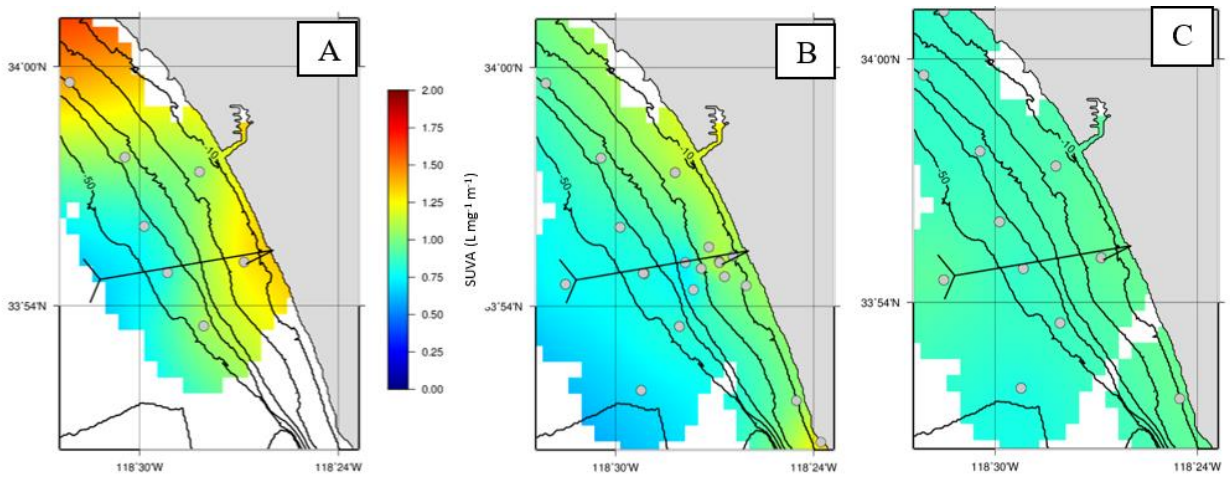

Figure 10. $SUVA_{254}$ values obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

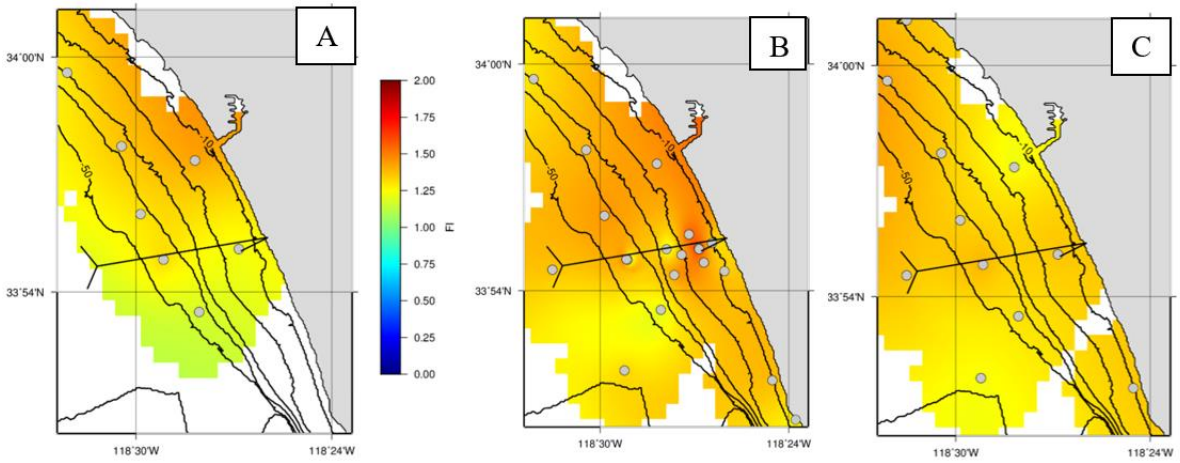

Figure 11.Fluorescence index values obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Prediversion stage, B) Diversion stage, and C) Post-diversion.

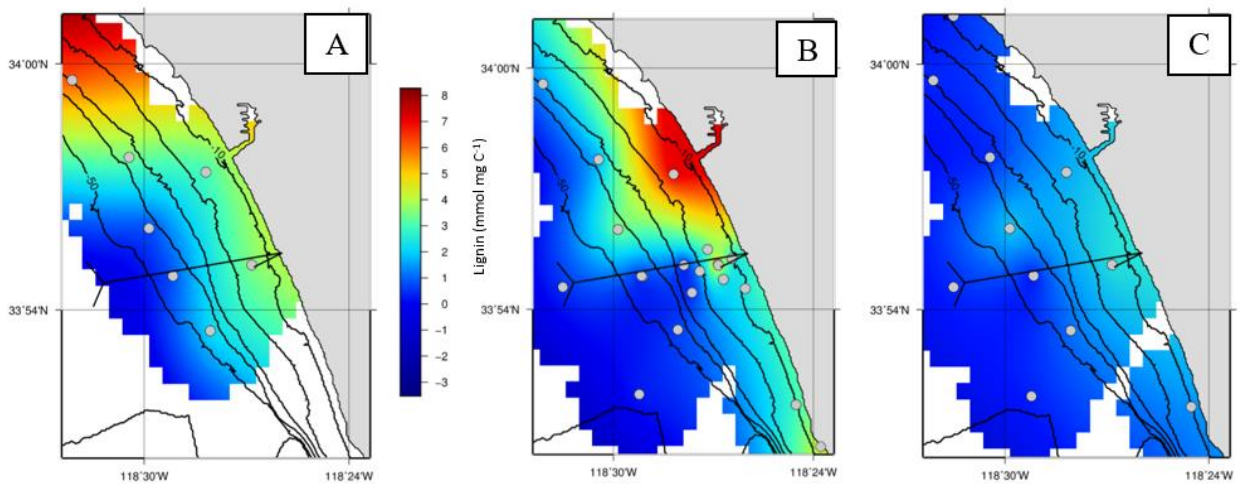

Figure 12. Lignin values obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Pre-diversion stage, B) Diversion stage, and C) Post-diversion.

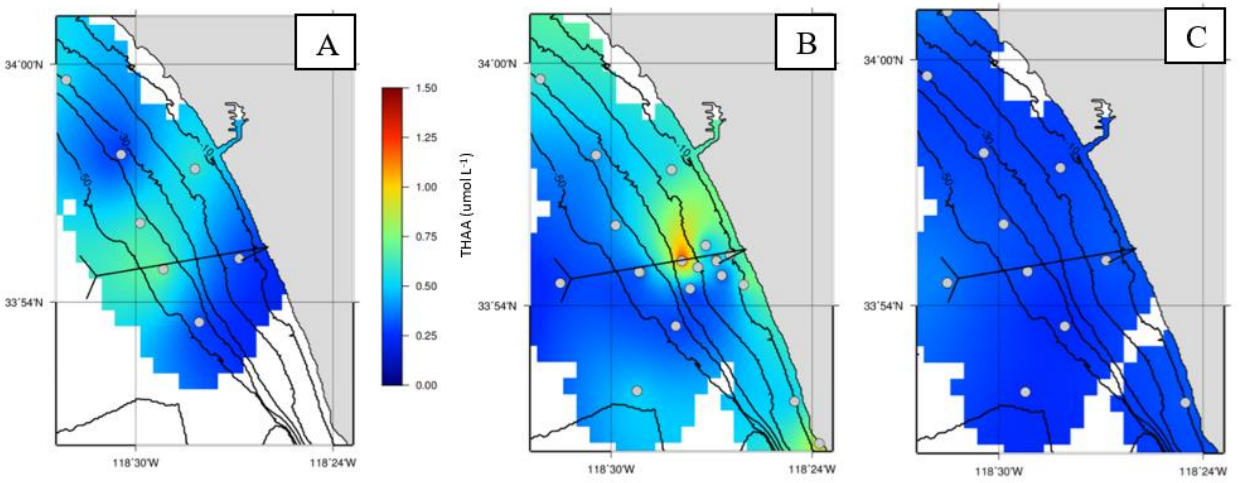

Figure 13. THAA concentrations obtained during the diversion project of the Santa Monica Bay, California separated based on stage: A) Prediversion stage, B) Diversion stage, and C) Post-diversion.

Distinct patterns were revealed during the individual stages. In general, optical parameters and concentrations of amino acids showed natural variations related to water mixing, wind direction, episodic run-off, and the influence of sewage effluent.

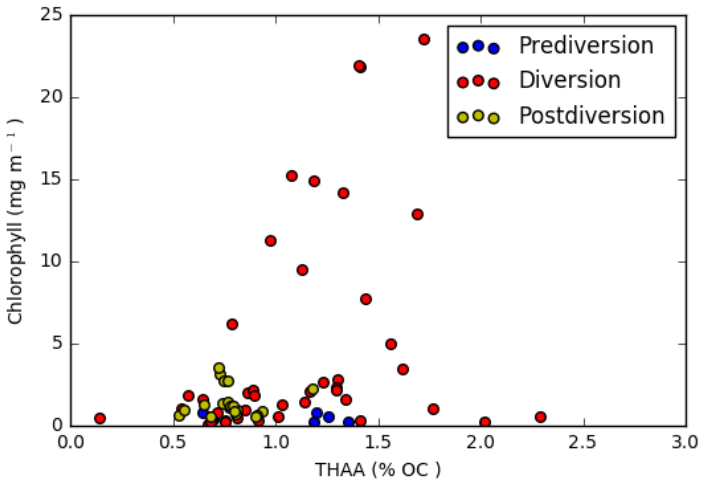

Figure 14. The relationship plots between the indicator, THAA, and the in situ value obtained for Chlorophyll.

Figure 14 shows the relationship of chlorophyll fluorescence with THAA yields. Although there was not a clear relationship between these two variables, during the diversion event higher chlorophyll was related to higher yields indicating the production of new DOM.

Table 1. Indicator and in situ data obtained during the Hyperion Water Reclamation Plant: Effluent Pumping Plant Header Replacement Project

Sample	Date	DOC (µmol L^{-1})	THAA (%OC)	$S_{275-295}$	S_R	Lignin[1] (mmol mg C^{-1})	SUVA (L mg^{-1} m^{-1})	BIX	FI	Chlorophyll[2] (mg m^{-3})	CDOM[3] (mg m^{-3})
D10W	11/11/2015	140	3.8	-0.032	2.1	1.2	0.9	1.3	1.3	0.9	0.1
D10W	11/5/2015	163	2.8	-0.029	2.0	2.0	0.9	1.3	1.3	3.1	0.4
D10W	10/14/2015	176	2.9	-0.027	1.6	4.6	1.0	1.2	1.3	1.1	0.2
D10W	10/21/2015	150	3.2	-0.035	2.1	0.7	0.8	1.2	1.1	0.8	0.0
D10W	9/16/2015	176	2.8	-0.028	1.7	2.1	1.1	1.0	1.2	0.4	0.8
D10W	9/30/2015	157	2.9	-0.042	3.0	0.2	0.7	1.2	1.2	0.3	-0.2
D11W	11/11/2015	142	4.3	-0.033	2.0	1.5	0.8	1.5	1.1	0.9	0.4
D11W	11/5/2015	155	3.0	-0.036	2.3	0.7	0.8	1.2	1.3	0.6	0.0
D11W	10/14/2015	147	3.6	-0.041	2.5	0.4	0.7	1.6	1.2	0.3	-0.3
D11W	9/30/2015	155	2.8	-0.043	3.0	0.2	0.7	1.5	1.5	0.2	-0.2
D13W	11/11/2015	154	3.3	-0.029	2.0	1.9	1.0	1.2	1.4	1.4	1.0
D13W	10/14/2015	178	2.9	-0.030	1.9	1.7	0.9	1.3	1.4	1.8	0.3
D13W	10/21/2015	211	2.5	-0.023	1.5	4.6	1.2	1.2	1.3	7.8	1.4
D13W	9/30/2015	264	1.8	-0.023	1.8	2.9	1.0	1.1	1.4	21.9	2.6
D1W	11/11/2015	152	3.9	-0.031	2.1	1.2	0.9	1.2	1.3	2.3	0.5
D1W	11/5/2015	159	2.8	-0.032	2.2	1.1	0.8	1.1	1.4	1.0	0.4
D2W	11/11/2015	145	3.6	-0.031	2.2	1.2	0.9	1.3	1.5	1.2	0.3
D2W	11/5/2015	156	2.9	-0.032	2.1	1.1	0.8	1.2	1.4	1.2	0.4
D2W	10/14/2015	222	2.2	-0.025	1.7	2.8	1.0	1.1	1.4	5.0	1.3
D2W	10/21/2015	165	2.9	-0.030	2.0	1.5	0.9	1.1	1.3	1.4	0.6
D2W	9/16/2015	214	2.4	-0.022	1.4	6.1	1.4	0.8	1.3	0.8	1.4
D2W	9/30/2015	213	2.3	-0.031	2.2	0.8	0.8	1.2	1.3	1.6	0.2
D3W	9/16/2015	161	3.1	-0.033	1.7	0.9	0.8	1.1	1.2	0.4	0.0
D4W	11/11/2015	141	3.9	-0.031	2.1	1.3	0.9	1.5	1.3	0.7	0.4
D4W	11/5/2015	155	2.9	-0.033	2.2	0.9	0.8	1.2	1.4	1.4	0.3
D4W	10/14/2015	193	2.5	-0.029	2.0	1.6	1.0	1.2	1.4	2.8	0.7
D4W	10/21/2015	173	2.8	-0.028	1.9	1.9	0.9	1.2	1.6	1.3	2.0
D4W	9/16/2015	184	2.7	-0.025	1.4	3.4	1.1	0.9	1.4	0.3	0.9
D4W	9/30/2015	181	2.7	-0.033	2.5	0.6	0.8	1.2	1.4	2.0	0.3
D5W	11/11/2015	155	3.4	-0.029	2.0	1.6	0.9	1.2	1.3	1.2	0.8
D5W	11/5/2015	165	2.7	-0.028	1.9	2.6	0.9	1.1	1.2	1.3	0.6
D5W	10/14/2015	222	2.2	-0.020	1.4	10.1	1.1	1.0	1.5	12.9	1.6
D5W	10/21/2015	197	2.3	-0.022	1.5	7.2	1.1	1.0	1.5	2.1	2.6
D5W	9/16/2015	187	2.7	-0.026	1.5	2.9	1.0	1.0	1.4	0.6	1.7
D5W	9/30/2015	235	2.1	-0.024	1.9	2.9	1.1	1.1	1.4	14.2	2.0
D6W	11/11/2015	145	3.7	-0.029	1.9	2.7	0.9	1.1	1.3	0.6	0.4
D6W	11/5/2015	159	2.9	-0.029	2.0	2.1	0.9	1.2	1.4	2.7	0.4
D6W	10/14/2015	160	3.1	-0.030	1.7	3.7	0.8	1.3	1.4	0.5	0.4

D6W	10/21/2015	166	2.8	-0.028	1.6	3.4	0.9	1.1	1.5	1.8	0.6
D6W	9/16/2015	159	3.2	-0.035	2.1	0.7	0.8	1.1	1.3	0.3	-0.1
D6W	9/30/2015	169	2.8	-0.035	2.7	0.5	0.7	1.3	1.3	0.6	-0.1
D7W	11/11/2015	139	3.9	-0.034	2.2	1.0	1.1	1.3	1.4	0.6	0.0
D7W	11/5/2015	155	3.0	-0.033	2.1	1.3	0.8	1.3	1.3	0.6	0.0
D7W	10/14/2015	177	3.6	-0.034	2.2	0.7	0.8	1.5	1.4	0.5	0.4
D7W	10/21/2015	147	3.2	-0.038	2.1	0.5	0.8	1.2	1.4	0.3	-0.1
D7W	9/30/2015	159	2.8	-0.041	2.4	0.0	0.7	1.5	1.1	0.1	-0.1
D8.5W	10/26/2015	168	2.7	-0.042	2.2	0.3	0.7	1.4	1.2	0.1	NaN
D8W	11/5/2015	159	2.9	-0.032	2.2	1.0	0.8	1.3	1.4	3.5	0.4
D8W	10/14/2015	161	3.2	-0.034	2.2	0.5	0.8	1.1	1.5	0.5	-0.1
D8W	10/21/2015	167	3.2	-0.021	1.1	0.5	1.0	1.2	1.4	1.0	-0.4
D8W	10/26/2015	195	2.5	-0.037	1.9	0.7	0.9	1.1	1.0	0.2	NaN
D8W	9/16/2015	159	3.1	-0.035	2.0	0.8	0.8	1.0	1.3	0.3	-0.2
D8W	9/30/2015	157	2.8	-0.042	2.4	0.2	0.7	1.4	1.4	0.3	-0.2
D9.5W	10/26/2015	170	2.7	-0.039	2.1	0.4	0.7	1.1	1.4	0.2	NaN
D9W	11/11/2015	153	3.4	-0.026	1.8	3.7	1.0	1.3	1.3	0.9	0.7
D9W	11/5/2015	167	2.7	-0.029	2.0	1.6	0.9	1.2	1.4	2.8	0.7
D9W	10/14/2015	284	1.6	-0.021	1.5	6.1	1.2	1.0	1.7	2.3	12.9
D9W	10/21/2015	230	2.0	-0.023	1.6	4.2	1.2	1.1	1.6	2.7	8.7
D9W	10/26/2015	226	2.2	-0.026	1.7	2.2	0.9	0.9	1.5	0.6	NaN
D9W	9/16/2015	183	2.9	-0.023	2.0	3.5	1.3	0.9	1.2	0.8	1.0
D9W	9/30/2015	350	1.3	-0.020	1.4	6.2	1.2	0.9	1.7	3.5	12.1
DD2B	9/30/2015	249	2.0	-0.024	2.0	2.5	1.0	1.2	1.3	21.9	3.1
DDIC	10/14/2015	216	2.3	-0.026	1.8	2.3	1.0	1.1	1.6	1.6	5.4
DDIC	10/21/2015	191	2.9	-0.026	1.8	2.3	1.1	1.3	1.3	11.3	1.5
DOB	10/21/2015	207	2.5	-0.025	1.7	3.0	1.1	1.1	1.3	14.9	2.5
DOB	9/30/2015	216	2.3	-0.027	2.2	1.7	0.9	1.9	1.3	15.3	2.0
DOD	10/14/2015	235	2.1	-0.025	1.8	2.8	1.1	1.1	1.6	2.1	3.3
DOD	10/21/2015	174	2.9	-0.029	2.0	1.5	1.0	1.2	1.4	6.2	0.6
DOD	9/30/2015	166	2.8	-0.037	2.7	0.4	0.7	1.3	1.2	1.1	0.0
DUIC	10/14/2015	228	2.3	-0.025	1.7	3.4	1.1	1.0	1.6	2.2	1.8
DUIC	10/21/2015	206	2.5	-0.025	1.6	2.8	1.1	1.3	1.6	9.5	3.2
ZONE 4KH	10/21/2015	221	2.6	-0.002	1.5	4.3	1.3	1.1	1.3	23.5	2.4

[1]Lignin values are the $TDLP_9$
[2]SeaBird WEDSTAR ECO-AFL chlorophyll sensor
[3]SeaBird WETSTAR CDOM sensor

CHAPTER IV

DISCUSSION

Santa Monica Bay is a dynamic coastal ecosystem where water properties, and distribution of nutrients and DOM are controlled by wind mixing, upwelling, biological production and run-off. The Hyperion Treatment Plant discharges about 250 million gallons of treated effluent during normal operation to Santa Monica Bay. The required maintenance of the 5-Mile Outfall redirected discharge of treated wastewater to a one-mile emergency outlet that was located in much shallower, warmer water. Given the proximity of the discharge to beaches and areas used for recreation, the potential for harmful algae blooms, deterioration of water quality, and associated risk to human health was high and required an extensive monitoring program.

Sources of DOM in Santa Monica Bay

One important aspect of this study was to study the temporal and spatial evolution of DOM sources in Santa Monica Bay. DOM components affect ocean color signatures that can be effectively measured by satellite-borne sensors. Proper calibration of ocean color signatures to absorbing DOM components are a critical step towards the application of remote sensing methods for water quality monitoring in coastal ecosystems.

Several distinct sources of DOM were present in Santa Monica Bay surface waters and could be distinguished through analysis of amino acids and optical properties. The presence of terrestrial-derived DOM (tDOM) was indicated by increased abundances of aromatic structures such a lignin. Lignin is a unique structural biopolymer that only occurs in vascular plants (Hedges and Mann, 1979). As expected, abundance of terrestrial DOM was highest close to the

shore, indicating run-off from episodic rain events. The diversion event coincided with a major rain event and resulted in a visible pulse of tDOM at Marina del Rey. Marina del Rey is home to the last wetland area in the Los Angeles basin and contains the end of a flood control channel. The data also indicated a pulse of tDOM before the diversion of effluent north of Marina del Rey towards the Santa Monica Mountains.

Offshore DOM signatures in surface waters were dominated by marine sources reflection biological production and remineralization processes. Water dynamics in Santa Monica Bay follow a seasonal cycle driven by the direction of winds. Upwelling occurs during April/May bringing cold, DOC-depleted but nutrient-rich waters to the surface. Nutrient input leads to episodic phytoplankton blooms adding new DOM to surface waters. After the upwelling seasons, surface waters in Santa Monica Bay stratify and photosynthesis and remineralization processes determine DOM sources.

The input of phytoplankton-derived DOM was clearly indicated by elevated THAA yields—1-3 %OC. For comparison, THAA yields in oligotrophic region of the large ocean gyres are < 1% OC (Kaiser and Benner, 2008). Amino acid sources contribute to optical properties of surface waters mainly due to the aromatic amino acids tyrosine, phenylalanine, and tryptophan. An additional sewage-derived DOM source was indicated by optical properties in close proximity to the end of the pipe. Effluent DOM underwent primary and secondary treatment processes before release. Such processes alter DOM composition and structure. Secondary treatment of sewage effluent included disinfection with sodium hypochlorite, which was continuously monitored to ensure proper dosage. In effect, disinfection resulted in bleaching of sewage DOM altering optical characteristics in particular absorption typical of aromatic structures.

A small increase in lignin concentrations in the sewage plume could be related to residual vascular plant derived DOM in the effluent or other aromatic compounds with similar optical characteristics. For example, spices, food flavors, and personal care products can be an ample source of vanillin that ends up in sewage and survives bleaching by hypochlorite (Salemme et al., 2012). To resolve distinct sources of sewage DOM and their correlation with optical properties additional molecular analysis are necessary.

Water Quality in Santa Monica Bay

In general, water quality along Santa Monica beaches is high during the dry, summer weather but deteriorates during wet weather conditions as storm drains deliver polluted waters to the ocean (Heal the Bay 2015-2016 Beach Report Card). The Heal the Bay 2015-2016 Beach Report Card graded Santa Monica as one of the beaches with the highest water quality among beaches in Southern California. Excellent water quality along heavily urbanized shorelines is a result of continuously improving management strategies to retain storm waters, improved efficiencies of sewage treatment plants, and continuous monitoring programs.

The diversion of the effluent from HTP over six weeks in 2015 resulted in substantial degradation of water quality. At the beginning of the diversion, sightings of sanitary waste items and hypodermic needles occurred along the shoreline triggering short-term beach closures and cleanup efforts by the City of Los Angeles. An investigation discovered that the source of these sewage-derived objects were connected to an earlier spill over ten years ago. The earlier spill event discharged these objects into the one-mile pipe that were never properly flushed.

An additional concern was increased abundances of harmful bacteria (Heal the Bay 2015-2016 Beach Report Card). Monitoring of hypochlorite dosage revealed that there were large

variations in hypochlorite concentration, and this could have been responsible for bacterial abundances to exceed mandated thresholds (Heal the Bay 2015-2016 Beach Report Card). Effective management strategies generally maintain low nutrient concentrations in surface waters. However, during the diversion of sewage measureable concentrations of ammonium and phosphate were delivered to shallow, warm waters. As a result, phytoplankton proliferated affecting water color and quality.

In addition to effects from sewage discharge, natural rain events and associated storm water discharge impact water quality on a continuous basis. Measurements presented here provide simple tools to track water quality in coastal ecosystems and help inform public health agencies.

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